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Tricyclo[2.1.0.0^{2,5}]pent-3-ylidene: Stereoelectronic Control of Bridge-Flapping within a Nonclassical Nucleophilic Carbene

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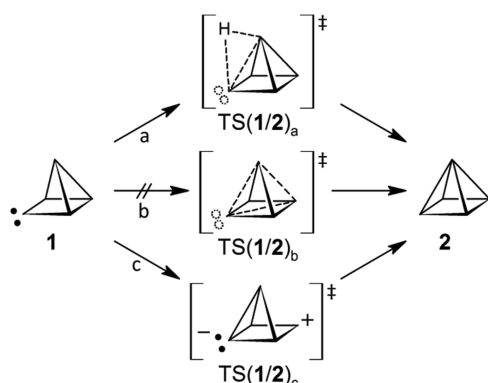ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

ABSTRACT: Tricyclo[2.1.0.0^{2,5}]pent-3-ylidene is a carbene foreseen to rearrange to pyramidane (c-C$_4$H$_4$)C, a highly strained molecule featuring an inverted C atom. Modeling of the carbene, using the (U)MPWB1K/cc-pVTZ//(U)MPWB1K/6-311G(d) theoretical model, indicated a large singlet−triplet energy gap ($\Delta E_{S-T} = -45$ kcal/mol), a high gas-phase proton affinity (PA = 258 kcal/mol), and a preference for electron-poor alkenes. These properties are consistent with those of nucleophilic carbenes. Structural differences between the C_s-symmetric singlet ($\omega_{flap} = \pm 44$ deg) and C_{2v}-symmetric triplet ($\omega_{flap} = 0$ deg) stem from nonclassical electron delocalization in the former and the lack thereof in the latter. Degenerate bridge-flapping of the singlet's main bridge, which comprises the reactive divalent C3 atom, is computed to be slow due to a high activation barrier of the C_{2v}-symmetric transition state (TS) ($E_a = 17$ kcal/mol). The position of the conformeric equilibrium is subject to stereoelectronic control. 1-Substituted derivatives of the carbene (R ≠ H) are sensitive to σ inductive effects. A *proximal* conformation is preferred when R is electron-donating and a *distal* one is favored when R is electron-withdrawing. Finally, carbene rearrangements via 1,2-C atom shift or enyne fragmentation were computed. The C_{2v}-symmetric bridge-flapping TS has the proper geometry to initiate enyne fragmentation.
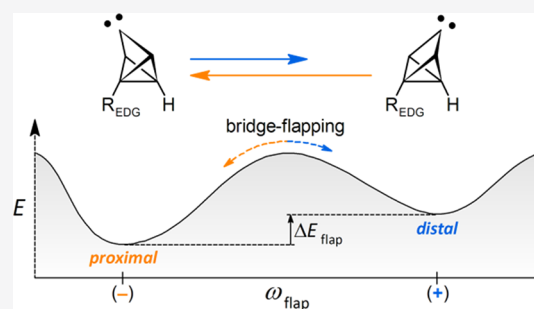
INTRODUCTION

Tricyclo[2.1.0.0^{2,5}]pent-3-ylidene (**1**)[1−12] is an enigmatic carbene[13−29] accessible only, as yet, via computational modeling.[30] The reactive intermediate has garnered much interest as a possible precursor to pyramidane (**2**),[2−11,31,32] an elusive target featuring an inverted C atom.[33,34] Direct reaction of **1** to **2** has been posited to occur either by 1,3-C−H bond insertion via TS(**1/2**)$_a$ (Scheme 1, path a)[5] or by C−C bond insertion via TS(**1/2**)$_b$ or TS(**1/2**)$_c$ (Scheme 1, paths b and c).[5,35] Pericyclic TS(**1/2**)$_b$ is unlikely (Scheme 1, path b),[22]

however, because a cheletropic reaction within **1** between its C3 atom and C1−C5 bond suffers from orbital misalignment.[22,36] In contrast, the elementary step **1** → **2** via zwitterionic TS(**1/2**)$_c$ (Scheme 1, path c),[3,5] which stems from C−C bond heterolysis, is the likely mechanism because TS(**1/2**)$_c$ is lower in energy than TS(**1/2**)$_a$.

The potential role of **1** in pyramidane chemistry has been amply documented.[2−11] In contrast, little is known about the carbene's innate character. Thus, key properties of **1** and pertinent structures are computed in this report. These include the following: (1) singlet−triplet energy gap (ΔE_{S-T}),[37−39] (2) gas-phase proton affinity (PA),[40,41] (3) hard−soft acid−base (HSAB) parameters,[42−45] and (4) carbene−alkene cyclo-addition $\Delta\Delta E$ values.[46−50] These data help classify the reactive nature of carbenes (e.g., (+)-electrophilic, (−)-nucleophilic, or (±)-ambiphilic).[44−52]

Dialkylcarbenes undergo rapid 1,2-H atom shift reactions if a suitable α-C−H bond is present.[53−55] This would give tricyclo[2.1.0.0^{2,5}]pent-2-ene (**3**) in the case of **1** (Scheme 2a) and adamantene (**5**)[56−60] in the case of adamantylidene

Scheme 1. Posited Rearrangements of Carbene 1 to Pyramidane (2)

Scheme 2. [1,2]-Sigmatropic Rearrangements of Polycyclic Carbenes 1 and 4 Give Bridgehead Alkenes

Scheme 3. Bridge-Flapping Equilibria within Substituted Polycyclic Carbenes 1-R and 4-R
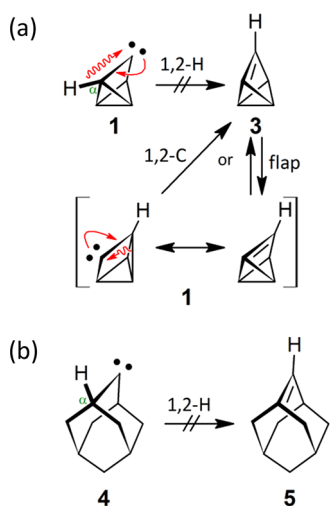
$(4)^{60−65}$ (Scheme 2b). Carbene **4** does not yield **5**, however, because the bridgehead C−C double bond violates Bredt's rule.[66−69] Strain within **5**, caused by the severely distorted π bond, impedes **4** → **5**. Orbital alignment is also unfavorable. The divalent C2 atom's empty p orbital is orthogonal to the α-C−H bonds within **4**. These factors contribute to a high $\Delta G^{‡}_{4→5}$, computed to be 52.7 kcal/mol.[60] Instead of a 1,2-H atom shift, **4** reacts via a 1,3-C−H bond insertion reaction (cf. Scheme 1, path a), requiring only 11.8 kcal/mol.[60] Thus, orbital misalignment (Figure 1a) should preclude **1** → **3** via a
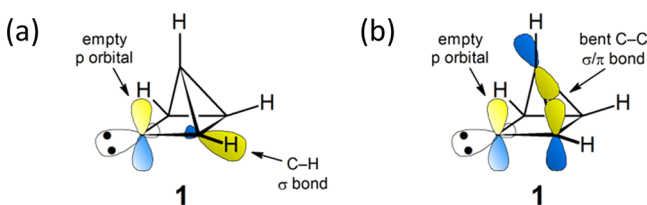

Figure 1. [1,2]-Sigmatropic rearrangements within carbene **1** depend on orbital alignment; (a) 1,2-H atom shifts should not be possible, but (b) 1,2-C atom shift should proceed (cf. Scheme 2).

1,2-H atom shift (Scheme 2a), while orbital alignment (Figure 1b) should foster **1** → **3** via a 1,2-C atom shift reaction (Scheme 2a). Indeed, this may be so efficient that **1** and **3** may actually be mesomers (i.e., [**1** ↔ **3**]) and not isomers (i.e., **1** ⇌ **3**). The possibility is explored in this report.

Singlet adamantylidene (^{1}**4**) has a C_{s}-symmetric equilibrium geometry and undergoes degenerate bridge-flapping via C_{2v}-symmetric TS(**4/4**)$_{flap}$ (Scheme 3a).[60,62−65] An analogous conformeric equilibrium has been computed for **1** (Scheme 2a), but its E_{a} is considerably higher.[4−7] Another possible similarity between carbenes **1** and **4** has to do with the conduction of stereoelectronic effects through their polycyclic C-atom frameworks.[64] An example of this is shown for *prox*-**4**-R, where R is an EDG (Figure 2). The potential for **1** to do this is investigated by comparing 1-substituted tricyclo-[2.2.1.0^{2,5}]pent-3-ylidenes (**1**-R; Scheme 3b) with γ-substituted adamantylidenes (**4**-R; Scheme 3a).[64,65]
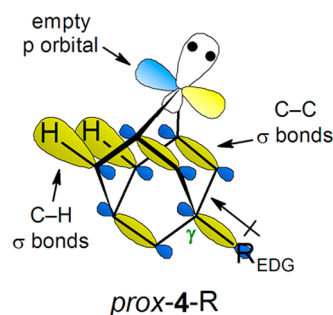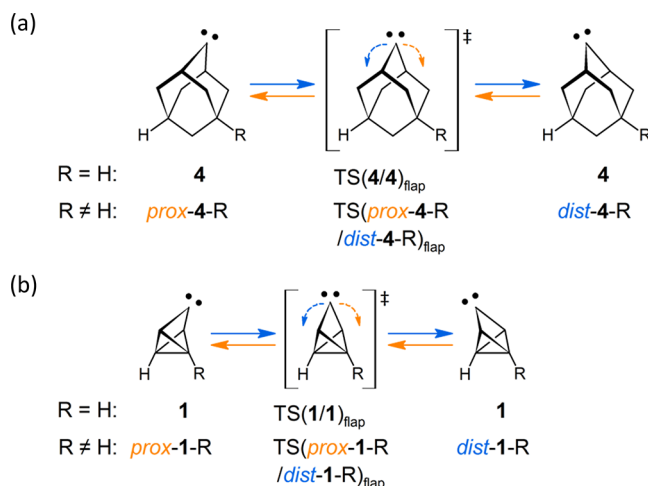

Figure 2. γ-Substituted adamantylidenes (**4**-R) exhibit stereo-electronic effects based on proper orbital alignment and the σ inductive effect of R (e.g., R$_{EDG}$).

■ RESULTS AND DISCUSSION

The (U)MPWB1K/cc-pVTZ//(U)MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model was used to compute equilibrium geometries, transition state (TS) geometries, single-point energies, zero-point vibrational energy (ZPVE) values, and intrinsic reaction coordinates (IRCs). The MPWB1K method was chosen because it gives accurate activation energy (E_{a}) values for carbene reactions.[70−72] The theoretical model's suitability was tested by comparing relevant TS and E_{a} results against the reported ones:[2,3,5,7] (1) **1** → [TS(**1/2**)$_{a}$]‡ → **2** (Scheme 1, path a) and (2) **1** → [TS(**1/2**)$_{c}$]‡ → **2** (Scheme 1, path c). The 1,3-C−H bond insertion reaction (Scheme 1, path a) was modeled using MPWB1K and MP2 since MP2 was used in an earlier report:[5] E_{a} = 32.7[73] and 33.5[74] kcal/mol. The transition state TS(**1/2**)$_{a}$ was confirmed herein by an IRC (see the Supporting Information) and leaves no doubt that the earlier E_{a} is erroneous.[7,73] The conversion of **1** to **2** via zwitterionic TS(**1/2**)$_{c}$ (Scheme 1, path c) requires much less energy: E_{a} = 2.2,[4,5,7] 3.5,[2,3] and 5.2[74] kcal/mol. The transition state TS(**1/2**)$_{c}$ was confirmed by a plateau-type IRC (see the Supporting Information), which can indicate ring opening within strained hydrocarbons.[75]

The computed structures for ^{1}**1**, ^{3}**1**, TS(**1/2**)$_{a}$, and TS(**1/2**)$_{c}$ are presented in Figure 3a−d. Fundamental properties of carbene **1**, such as $\Delta E_{S−T}$, were computed (Table 1). The difference between the computed and experimental $\Delta E_{S−T}$ values for CH$_{2}$ was used to obtain corrected $\Delta E_{S−T}$ values (eq
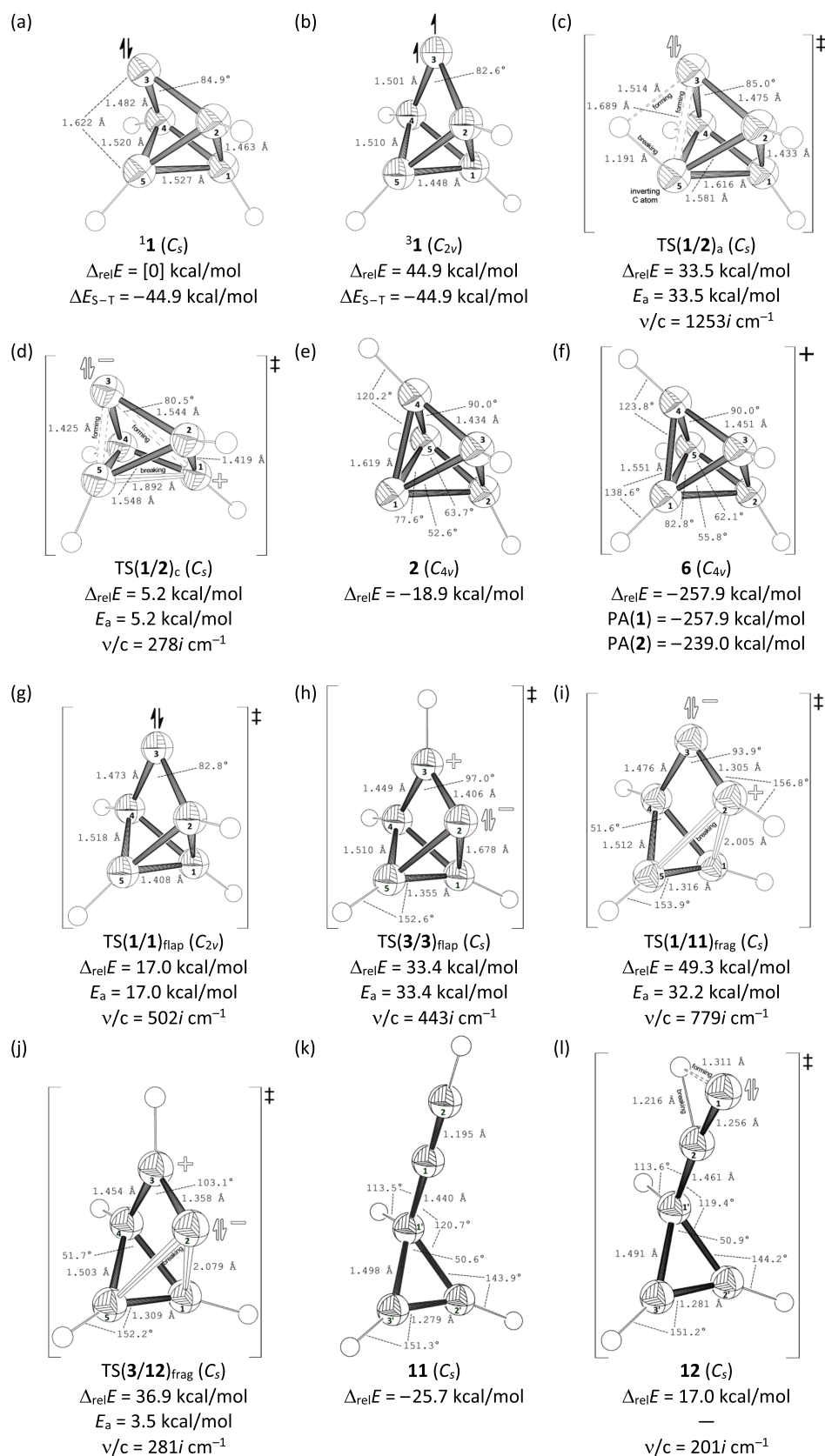
Figure 3. (a−l) Structures of **1**, **2**, **3**, **6**, **11**, **12**, and related molecules computed using the (U)MPWB1K/cc-pVTZ//(U)MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model. (ORTEP structures are 50% ellipsoids.)

1). The singlet ground state ^{1}**1** is 45 kcal/mol below the triplet state ^{3}**1**. The remarkably large ΔE_{S-T} is due to two factors.

First, ^{3}**1** is destabilized because the bond angle θ_{carbene}, centered on the divalent C3 atom, is exceedingly small at

Table 1. Singlet vs Triplet Carbene 1[a]

Carbene Aspect/Property	$^1\mathbf{1}$	$^3\mathbf{1}$
spin multiplicity (2S + 1)	1	3
electron configuration	$^1(\sigma^2 p^0)$	$^3(\sigma^1 p^1)$
symmetry point group	C_s	C_{2v}
$\theta_{carbene}$[b]	84.9	82.6
$\Delta_{rel}E$	$[0]$[c]	44.9 kcal/mol[c]
ω_{flap}[d]	±43.5 deg	0 deg

[a]Computed using the (U)MPWB1K/cc-pVTZ//(U)MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model. [b]Bond angle of C2−C3−C4. [c]$\Delta E_{S-T} = -44.9$ kcal/mol. [d]$\omega_{flap} = \frac{1}{2}[\omega(C1-C2-C4-C3) - \omega(C5-C4-C2-C3)]$.

just 83 deg. This is far less than that in free $^3CH_2$ (i.e., 134 deg).[30,76,77] Second, $^1\mathbf{1}$ is stabilized by propitious orbital alignment within a bent C_s-symmetric structure. The considerable ΔE_{S-T} of −45 kcal/mol strongly suggests that $^1\mathbf{1}$ is a nucleophilic carbene. This classification is somewhat paradoxical since the reactive C3 atom of $\mathbf{1}$ is formally hypovalent.[78]

$$\Delta E_{S-T} = \Delta E_{S-T(comp)} - 4.6 \text{ kcal/mol} \qquad (1)$$

The main bridge of C_s-symmetric $^1\mathbf{1}$, which comprises the reactive divalent C3 atom, is torsionally bent by $\omega_{flap} = \pm43.5$ deg from the σ_v mirror plane within C_{2v}-symmetric $^3\mathbf{1}$,[74] which also exists within $TS(\mathbf{1/1})_{flap}$. The degenerate conformerism $^1\mathbf{1} \rightleftharpoons [TS(\mathbf{1/1})_{flap}]^{\ddagger} \rightleftharpoons ^1\mathbf{1}$ (Scheme 3b; R = H) entails a b_1-

symmetric vibration $\nu/c = 502i$ cm^{-1}) wherein the C3 atom flaps toward and away from C1 (Scheme 3b). Bridge-flapping within $^1\mathbf{4}$ is well established (Scheme 3a).[60,63,64] Its main bridge is bent to a lesser extent: $\omega_{flap} = \pm15.1$,[64,65] ±18.5,[63] and ±19.7[74] deg.

Table 2 lists important aspects for carbenes $\mathbf{1}$ and $\mathbf{4}$. They share many similar properties, such as symmetry, ground-state multiplicity, polarity, $prox \rightleftharpoons dist$ flapping equilibria, and gas-phase PA values that are comparable to those of other nucleophilic carbenes. Given these similarities, carbenes $\mathbf{1}$-R should exhibit π-facial selectivity, as with carbenes $\mathbf{4}$-R, because tilting of the main bridge exposes one side while shielding the other.[64,65]

However, there are some distinct differences between carbenes $\mathbf{1}$ and $\mathbf{4}$ (cf. Table 2). The bond angle $\theta_{carbene}$ centered on the divalent C atom of $\mathbf{1}$ is much lower than that of $\mathbf{4}$. This leads to ΔE_{S-T} values for $\mathbf{1}$ and $\mathbf{4}$ that are vastly different, as mentioned (Table 1). The $prox \rightleftharpoons dist$ flapping rate for $\mathbf{1}$ will be much slower than that for $\mathbf{4}$, especially at low temperatures. This is inferred from their disparate E_a values (Table 2). Thus, product selectivities based on reaction kinetics will differ greatly for $\mathbf{1}$ and $\mathbf{4}$.[64] Carbene $\mathbf{1}$ is not anticipated to undergo diastereoselective C−H bond insertion reactions despite its π-facial selectivity. In contrast to $\mathbf{4}$, $\mathbf{1}$ lacks the axial β C−H bonds that sterically orient the intermolecular transition states computed for $\mathbf{4}$.[64,65]

Carbene $\mathbf{1}$ has a gas-phase PA of 258 kcal/mol (Table 2 and eq 2). This is in the range of N-heterocyclic carbene (NHC) ylides.[40,78–83] Its PA is unusually high for a hydrocarbon and exceeds that of $\mathbf{2}$ (PA = 231,[7,84] 233,[7] and 239[74] kcal/mol) by their $\Delta_f H°$ difference. That is because they share the same conjugate acid,[40,41] C_{4v}-symmetric carbocation $\mathbf{6}$ (Scheme 4).

Table 2. Key Comparisons between Carbenes 1-R and 4-R[a]

Carbene Aspect/Property	prox-**1**-R (dist-**1**-R)	parent structure	prox-**4**-R (dist-**4**-R)
CH$_2$-groups (Σn)	0[b]		5
symmetry point group	C_s ($^1\mathbf{1}$)		C_s ($^1\mathbf{4}$)
	C_{2v} ($^3\mathbf{1}$)		C_{2v} ($^3\mathbf{4}$)
	C_{2v} (TS(**1/1**)$_{flap}$)		C_{2v} (TS(**4/4**)$_{flap}$)
$\theta_{carbene}$	85 deg ($^1\mathbf{1}$)		111 deg ($^1\mathbf{4}$)
	83 deg ($^3\mathbf{1}$)		118 deg ($^3\mathbf{4}$)
ΔE_{S-T}	−44.9 kcal/mol		−6.0 kcal/mol
dipole moment (μ)	4.2 D ($^1\mathbf{1}$)		2.6 D ($^1\mathbf{4}$)
	2.4 D ($^3\mathbf{1}$)		1.1 D ($^3\mathbf{4}$)
gas-phase PA	258 kcal/mol		265 kcal/mol
ω_{flap}	±43.5 deg[c]		±19.7 deg[d]
bridge-flapping ν/c	502i cm^{-1}		323i cm^{-1}
bridge-flapping E_a	17.0 kcal/mol		1.1 kcal/mol
$prox \rightleftharpoons dist$ rate	slower		faster
π-facial selectivity	yes		yes

[a]Computed using the (U)MPWB1K/cc-pVTZ//(U)MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model. [b]See ref 1 (a). [c]$\omega_{flap} = \frac{1}{2}[\omega(C1-C2-C4-C3) - \omega(C5-C4-C2-C3)]$. [d]$\omega_{flap} = \frac{1}{2}[\omega(C5-C3-C1-C2) - \omega(C7-C1-C3-C2)] = [180 \text{ deg} - \omega(C6-C3-C1-C2)]$.

Scheme 4. Protonation of 1 or 2 Gives Carbocation 6[a]
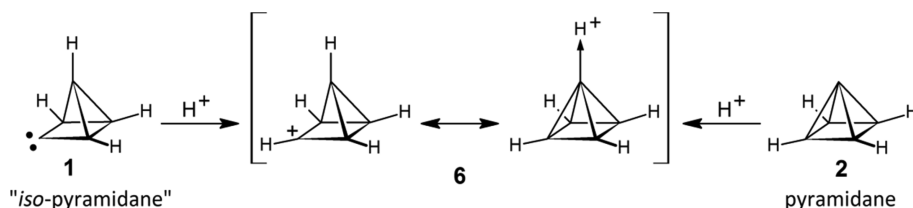
[a]Note that carbocation **6** represents both Brønsted−Lowry conjugate acids **1H**[+] and **2H**[+], which are identical to each other (i.e., **1H**[+] ≡ **2H**[+]), according to quantum chemical computations.

Indeed, one may view **1** as "*iso*-pyramidane" (i.e., **1** ≡ *iso*-**2**),[1d] because protonation of either **1** or **2** gives **6** (i.e., **1H**[+] ≡ **2H**[+] ≡ **6**; cf. Scheme 4).[2,9,10] This notion is also supported by comparing their frontier MOs.

$$PA = H°_B − H°_{BH^+} \text{ for B: } +H^+ → [B − H]^+ \quad (2)$$

An MO correlation diagram between [1]**1** and **2** has been reported at the MINDO/3 level of theory.[11,12] However, [1]**1** was treated as having C_{2v} symmetry[11] instead of the C_s symmetry found using ab initio methods. Thus, a new comparison was warranted. Frontier MO details for C_s-symmetric **1** are shown in Figure 4a,b and Table 3 and
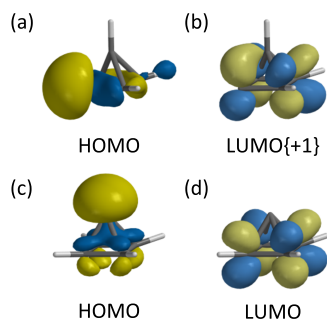
Figure 4. Frontier molecular orbitals for (a, b) carbene **1** and (c, d) pyramidane. Computed using the MPWB1K/cc-pVTZ//MPWB1K/6-311G(d) theoretical model (isosurface values = 0.064).

those for C_{4v}-symmetric **2** are found in Figure 4c,d and Table 4. The LUMO{+1} of **1** and LUMO of **2** are essentially the same. In contrast, their HOMOs are spatially different. The electron lone-pair density within each HOMO resides mainly in the protruding lobe of each one's σ orbital, whose position is governed by symmetry. These high-lying HOMOs are

ostensibly the source of the hydrocarbons' large gas-phase PA values. Note that the HOMO of **2** corresponds with the HOMO{−5} of **1** (Figure 5). Inspection of the HOMO{−1} level of **2** reveals a doubly degenerate pair of perpendicular MOs that feature in-between σ/π overlap (Table 4), which is the source of its banana-like bent bonds.[85,86] The degeneracy within **2** is broken in **1**, however, due to the presence of the carbene's electron lone pair, which is orthogonal in the HOMO{−1} but aligned in the HOMO{−2} (Table 3). Once again, **1** may be viewed as "*iso*-pyramidane" given these frontier MO similarities.[1d]

The very large $\Delta E_{S−T}$ value for **1** of −45 kcal/mol (Table 1) means that the ground state [1]**1** should react as a nucleophile. This can be demonstrated, for example, from pericyclic [$_\pi 2_s + _\omega 2_a$] cycloadditions[36] of **1** with a representative set of alkenes.[46−49] The smaller ΔE value for each of the two possible donor (D)−acceptor (A) interactions denotes which one is dominant (eqs 3 and 4):[49] (1) $D_{carbene}(\sigma)$ with $A_{alkene}(\pi^*)$ or (2) $D_{alkene}(\pi)$ with $A_{carbene}(p)$. The sign of the resulting $\Delta\Delta E$ value, found using eq 5, indicates whether the carbene acts as an (+)-electrophile or a (−)-nucleophile.[87] A 2-D chart comparing carbene **1** with other alkenophiles is then assembled to reveal philicity trends (Table 5).[51,52] They indicate that **1** is more nucleophilic than **4**,[88] **2**, and *dist*-**1**-Br and almost as nucleophilic as the nonclassically bent carbene bicyclo[2.2.1]hept-2-en-7-ylidene.[51,87,89−91]

$$\Delta E_{(\sigma→\pi^*)nucleophilic} = (E_{\pi^*} − E_\sigma) \quad (3)$$

$$\Delta E_{(p←\pi)electrophilic} = (E_p − E_\pi) \quad (4)$$

$$\Delta\Delta E = \Delta E_{(\sigma→\pi^*)nucleophilic} − \Delta E_{(p←\pi)electrophilic} \quad (5)$$

Stereoelectronic control has been modeled computationally and observed experimentally when carbene **4** bears the remote γ-substituent R.[64] Specifically, σ inductive effects bias the *prox*-

Table 3. Frontier MOs of Carbene 1 ("*iso*-Pyramidane")[a]

	HOMO{−2}	HOMO{−1}	HOMO	LUMO{+1}
Occupancy	⇅	⇅	⇅	—
Orbital	HOMO{−2}	HOMO{−1}	HOMO	LUMO{+1}
E	−9.31 eV	−9.18 eV	−6.74 eV	2.17 eV

[a]Computed using the MPWB1K/cc-pVTZ//MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model.

Table 4. Frontier MOs of Pyramidane (2)[a]

Occupancy	⇅	⇅	⇅	—
Orbital	HOMO{−1}	HOMO{−1}	HOMO	LUMO
E	−8.82 eV	−8.82 eV	−7.85 eV	2.07 eV

[a]Computed using the MPWB1K/cc-pVTZ//MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model.
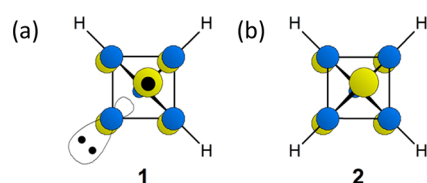

Figure 5. The (a) HOMO{−5} of carbene **1** corresponds to the (b) HOMO of pyramidane (**2**), according to the MPWB1K/cc-pVTZ// MPWB1K/6-311G(d) theoretical model.

4-R:*dist*-4-R ratio (cf. Scheme 3a). This, in turn, influences both intramolecular and intermolecular product selectivities (Table 6). The nature of R is the determining factor: (1) $\sigma_I < 0$ (−) if R = R_{EDG} and (2) $\sigma_I > 0$ (+) if R = R_{EWG}.[92] A similar

Table 6. Selective C–H Bond Insertions of γ-Substituted Adamantylidenes[a]

carbene 4-R	R_{EDG}	R_{EWG}
favored conformer	*prox*	*dist*
intramolecular[b]	*as*	*s*
intermolecular[c]	*anti*	*syn*

[a]cf. Ref 64. [b]Monosubstituted 2,4-didehydroadamantane product: asymmetric (*as*) or symmetric (*s*). [c]γ-Disubstituted adamantane solvolysis product: *anti* or *syn*.

situation for carbenes **1**-R was researched. Its bridge-flapping may be subject to σ inductive effects too. Note that carbenes **1**-R would not be diastereoselective, however, since they lack

Table 5. Differences in Frontier MO Energy Gaps (ΔΔE) between Carbenes and Alkenes[a,b]

Reactants	(D_2)	(C_s)	(D_{2h})	(C_s)	(C_s)	(C_{2h})
	5.55	4.12	3.33	3.19	0.87	−1.13
	5.31	3.88	3.09	2.95	0.63	−1.37
	1.92	0.49	−0.30	−0.44	−2.76	−4.76
	0.45	−0.98	−1.77	−1.91	−4.23	−6.23
	0.37	−1.06	−1.85	−1.99	−4.31	−6.31
	−0.75	−2.18	−2.97	−3.11	−5.43	−7.44
	−0.85	−2.28	−3.07	−3.21	−5.53	−7.53

[a]Computed using the MPWB1K/cc-pVTZ//MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model and eqs 3−5. [b]Units in eV.

sterically directing CH_2 groups. Moreover, their flapping equilibria are much slower. The bridge-flapping E_a for **1** (E_a = 12.8,[2,9] 13.5,[2,9] 14.6,[4,5,7] 16.2,[3] and 17.0[74] kcal/mol) is significantly higher than that for **4** (E_a = 1.1[74] kcal/mol).

Bridge-flapping transition states $TS(\mathbf{1/1})_{flap}$ and $TS(prox\text{-}\mathbf{1}\text{-}R/dist\text{-}\mathbf{1}\text{-}R)_{flap}$ were computed for **1** and a set of 1-substituted derivatives **1**-R, respectively, and verified by IRC analyses (Figure 6). Conformational effects caused by the following R-
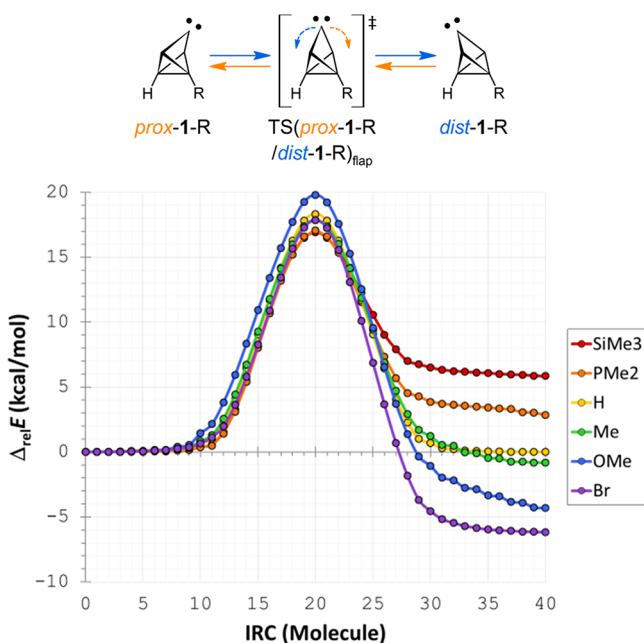
Figure 6. The *prox* ⇌ *dist* flapping equilibrium for carbenes **1**-R reverses if R_{EDG} is replaced by R_{EWG} (computed using the MPWB1K/6-311G(d)//MPWB1K/6-311G(d) theoretical model).

group substituents were explored: $SiMe_3$, PMe_2, H, Me, OMe, and Br. When R = H, the degenerate step $\mathbf{1} \rightarrow [TS(\mathbf{1/1})_{flap}]^{\ddagger} \rightarrow \mathbf{1}$ gives a symmetric curve since $\Delta E_{flap} = [0]$ (Figure 6). However, when R ≠ H, then $\Delta E_{flap} \neq 0$ (eq 6) because the distinct conformers *prox*-**1**-R and *dist*-**1**-R have different energies (i.e., $E_{prox} \neq E_{dist}$). For example, ΔE_{flap} increases by 4.3 kcal/mol with **1**-$SiMe_3$ but decreases by 6.7 kcal/mol with **1**-Br (cf. eq 6, Table 7, and Figure 6). The preference for a proximal or distal conformation is influenced by the σ inductive effect of substituent R, which can be quantified by a σ_I value.[92] Hence, a conformational bias based on the proximity of C3 to substituted C1 or unsubstituted C5 is observed. A proximal (*prox*) conformation is established when the divalent C atom (>C:) leans toward substituted C1, while a distal (*dist*) conformation exists when >C: is tilted toward

unsubstituted C5. It is evident from the energy profiles that *prox*-**1**-R is energetically preferred when R is an EDG, while *dist*-**1**-R is favored when R is an EWG. Hence, ΔE_{flap} decreases as R becomes more electron-withdrawing. These trends accord well with those of carbenes **4**-R.

$$\Delta E_{flap} = E_{dist} - E_{prox} \qquad (6)$$

The dipole moment of $^1\mathbf{1}$ (μ = 4.2 D) is high for a hydrocarbon. It is readily understood when one considers the intramolecular MO interaction between the carbene's empty p orbital and its high-lying HOMO{−1} (Table 3), which features bent C−C bonds having mixed σ/π-character (Figure 1b). Such donor−acceptor interactions are common within classical singlet carbenes (e.g., CCl_2) and nonclassical ones (e.g., bicyclo[2.2.1]hept-2-en-7-ylidene)[51,87,89−91] when the relevant orbitals are nearby, close in energy, and properly aligned. However, NHCs are such extreme examples of singlet carbenes that they are better described as ylides. The large ΔE_{S-T} value of −44.9 kcal/mol for **1** (Table 2) and the polycyclic carbene's reluctance to form the strained bridgehead alkene **5**, as depicted in Scheme 2a and Figure 1a, mean that the nonclassical carbene $^1\mathbf{1}$ has considerable ylidic character. Indeed, $^1\mathbf{1}$ is better described (and presented)[3] by the two equivalent resonance forms shown in Scheme 5. The singlet carbene is a "*gem*-zwitterion"[93] and its ylidic forms are 1,2-zwitterions. It is easy to see from Scheme 5 how $TS(\mathbf{1/2})_{\sigma}$, which is a 1,3-zwitterion with μ = 4.1 D, is readily attained from $^1\mathbf{1}$ (Scheme 1, path c; E_a = 2.2,[4,5,7] 3.5,[2,3] and 5.2[74] kcal/mol). In contrast, the ylidic nature of $^1\mathbf{1}$ might be responsible for the high relative energy of $TS(\mathbf{1/2})_a$ (Scheme 1, path a; E_a = 32.7[73] and 33.5[74] kcal/mol), which is less polar with μ = 2.8 D.

Carbene **1** and alkene **3** are functional isomers (i.e., $\mathbf{1} \rightleftharpoons \mathbf{3}$) according to classical force-field modeling (Figure 7a). However, they are identical molecules (i.e., $\mathbf{1} \equiv \mathbf{3}$) according to quantum chemical computations. They are not two species separated by a 1,2-C atom shift TS (i.e., no $\mathbf{1} \rightarrow [TS(\mathbf{1/3})]^{\ddagger} \rightarrow \mathbf{3}$), which explains why none could be found. Structures **1** and **3** are resonance forms of the same entity (i.e., $[\mathbf{1} \leftrightarrow \mathbf{3}]$). They share the same set of Cartesian coordinates and ylide resonance forms (Scheme 5). The equivalence of **1** and **3** points toward a key relationship between $TS(\mathbf{1/1})_{flap}$ (Figure 3g) and $TS(\mathbf{3/3})_{flap}$ (Figures 3h and 7c). The IRC for bridge-flapping within so-called **3** reveals that it is actually a reaction path for degenerate *transverse* bridge-flapping within **1** (Figure 8b). Drawing **1** in ylide form recasts the motion represented by the IRC as straightforward bridge-flapping.

Carbene **1** comprises (cyclopropyl)carbene (**7**)[94−102] and cyclobutylidene (**8**)[100−109] units and should react according to their known rearrangement types. Examples of these include

Table 7. Bridge-Flapping Equilibria of Carbenes 1-R[a]

R	$\omega_{flap,prox\text{-}\mathbf{1}\text{-}R}$ (deg)	$\omega_{flap,TS(prox\text{-}\mathbf{1}\text{-}R/dist\text{-}\mathbf{1}\text{-}R)}$ (deg)	$\omega_{flap,dist\text{-}\mathbf{1}\text{-}R}$ (deg)	$\Delta E_{flap,R}$[b] (kcal/mol)	$E_{a,prox\text{-}\mathbf{1}\text{-}R}$ (kcal/mol)	$E_{a,dist\text{-}\mathbf{1}\text{-}R}$ (kcal/mol)
$SiMe_3$	−42.5	0.8	41.4	4.3	15.8	11.4
PMe_2	−43.0	0.1	42.2	1.6	15.8	14.1
H	±43.5[c]	[0]	±43.5[c]	[0]	17.0[c]	17.0[c]
Me	−43.3	0.0	44.9	−1.5	16.8	18.3
OMe	−45.6	−0.2	45.9	−5.6	18.7	24.3
Br	−44.5	−1.4	44.7	−6.7	16.7	23.5

[a]Computed using the MPWB1K/cc-pVTZ//MPWB1K/6-311G(d) + (0.9513)ZPVE theoretical model. [b]See eq 6. [c]The *prox* and *dist* stereodescriptors do not apply when R = H.

Scheme 5. Nonclassically Delocalized Carbene 1 Is Polar and Gives Pyramidane (2) via Low-Barrier 1,3-Zwitterionic Transition State TS(1/2)$_c$[a]
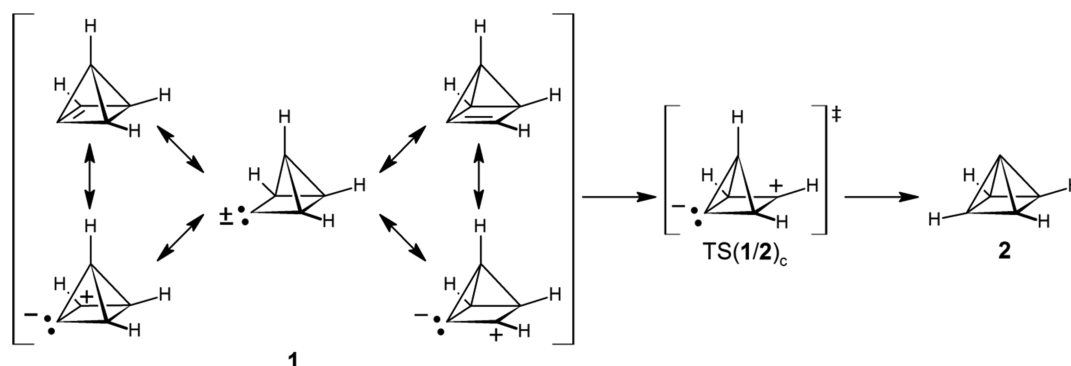
[a]Note that tricyclo[2.1.0.0^{2,5}]pent-3-ylidene (**1**) is identical to tricyclo[2.1.0.0^{2,5}]pent-2-ene (**3**), according to quantum chemical computations.
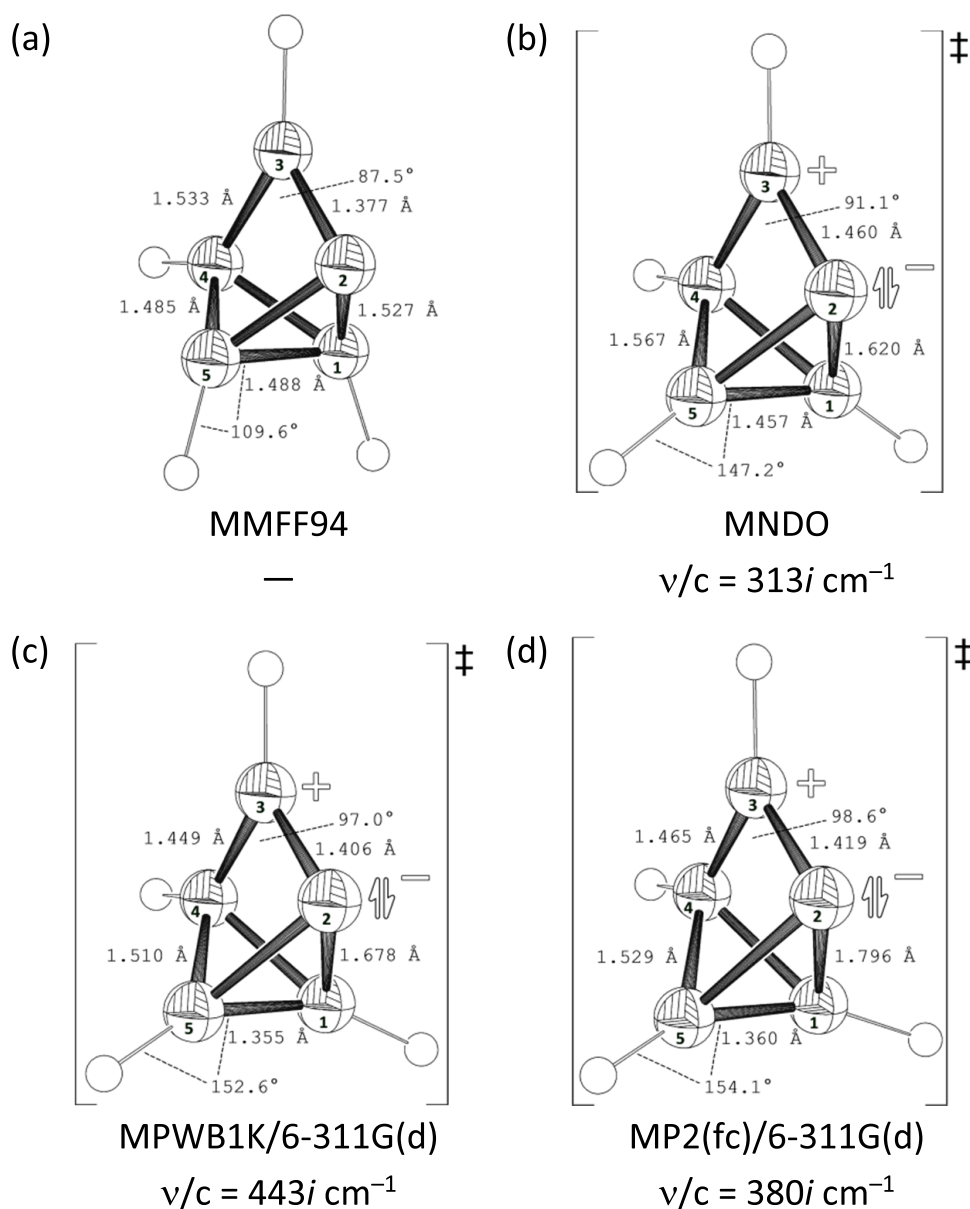
Figure 7. The bridgehead alkene tricyclo[2.1.0.0^{2,5}]pent-2-ene (**3**) was optimized with the (a) MMFF94 method and used as the starting geometry for (b−d) quantum chemical models, which were bridge-flapping transition states TS(3/3)$_{flap}$. (ORTEP structures are 50% ellipsoids.)
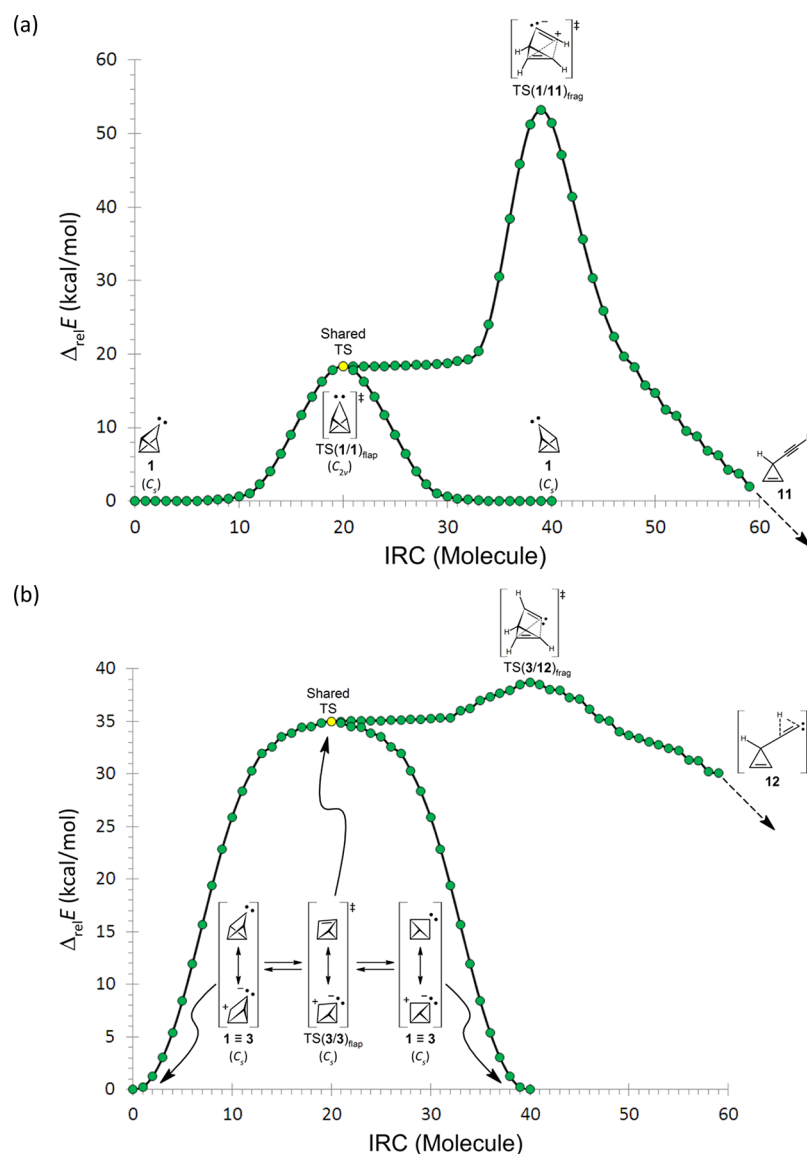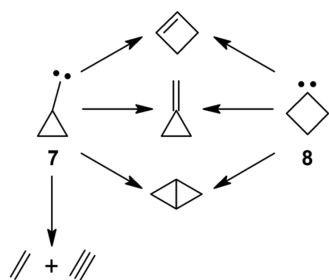
Figure 8. The yellow bifurcation points represent shared transition states. The combined IRCs show that (a) bridge-flapping TS($1/1$)$_{flap}$ is the starting point for enyne fragmentation to **11**, while (b) *transverse* bridge-flapping within **1**, or TS($3/3$)$_{flap}$, is the starting point for a different enyne fragmentation (MPWB1K/6-311G(d)//MPWB1K/6-311G(d)).

ring enlargement or ring contraction via a 1,2-C atom shift reaction and cyclopropanation via a 1,3-C−H bond insertion reaction (Scheme 6). (Cyclopropyl)carbenes can also react via enyne fragmentation reactions when structural circumstances are favorable. The most important of these is orbital

alignment.[96] The rigid C_s-symmetric carbene nortricyclylidene (**9**) is a perfect example of this and yields the C_s-symmetric enyne (cyclopent-3-en-1-yl)ethyne (**10**) almost exclusively (Scheme 7).[94−96] Presently, IRC calculations show that (cycloprop-2-en-1-yl)ethyne (**11**) is formed from the C_s-symmetric carbene [1]**1** via a shared TS,[75,110] namely, C_{2v}-symmetric TS($1/1$)$_{flap}$. At this bifurcation point, either bridge-flapping will continue or enyne fragmentation will commence toward TS($1/11$)$_{frag}$ (Scheme 8a and Figure 8a). Depictions of

Scheme 6. Rearrangements of (Cyclopropyl)carbene (7) and Cyclobutylidene (8)

Scheme 7. Enyne Fragmentation within Nortricyclylidene (9)
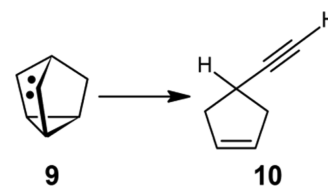
Scheme 8. Regular and Transverse Bridge-Flapping and Enyne Fragmentations for Carbene 1
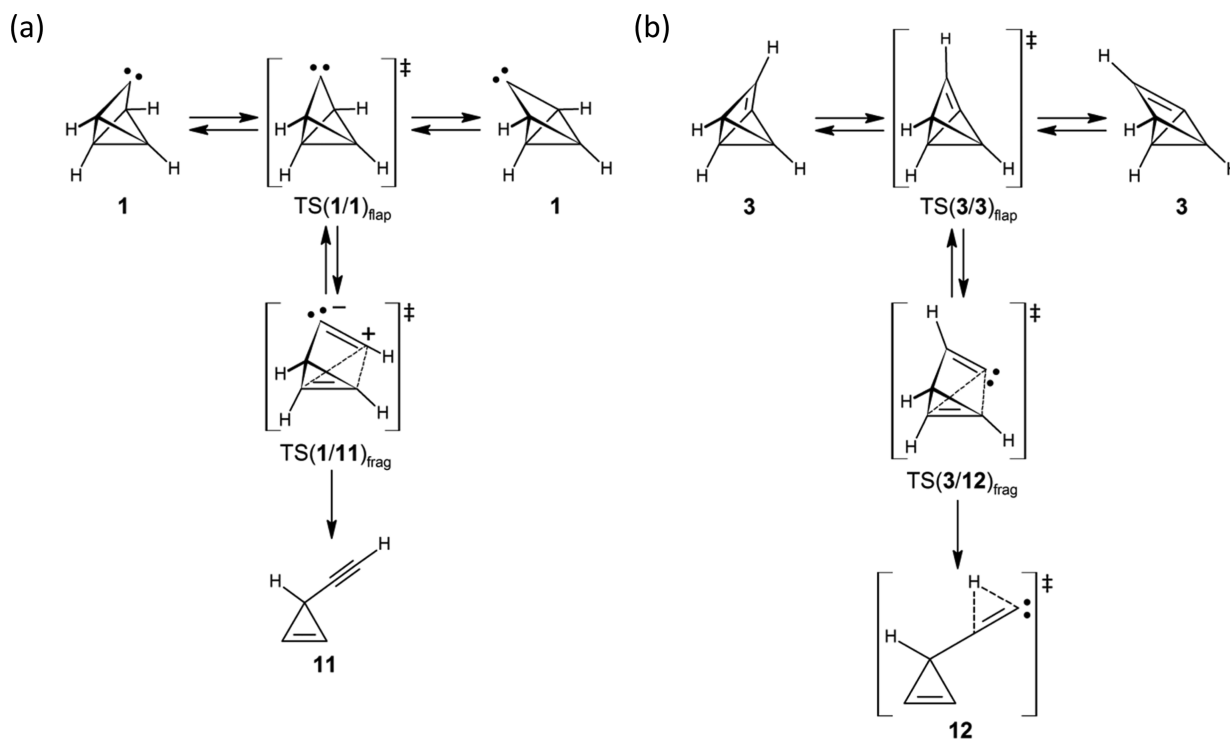
the properly aligned orbitals of the combined bridge-flapping/enyne fragmentation transition states are found in Figure 9.
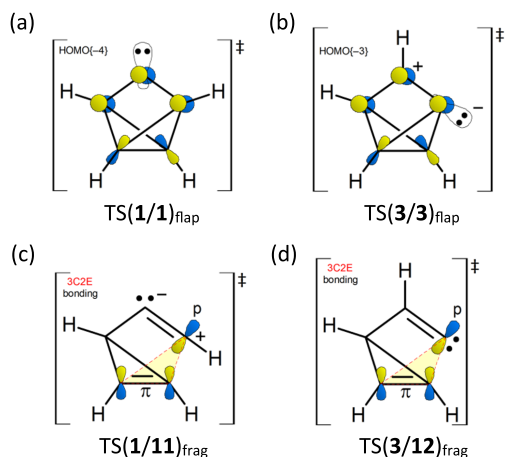
Figure 9. Important similarities between carbene **1** and alkene **3** are revealed from orbital descriptions of (a, b) bridge-flapping and (c, d) enyne fragmentation.

The Walsh orbitals of TS(**1**/**1**)$_{flap}$ (Figure 9a) and TS(**3**/**3**)$_{flap}$ (Figure 9b) combine with the p orbital of the divalent C atom and trivalent C atom, respectively, to give extended π-systems that stabilize the shared transition states. Stabilization is achieved also with TS(**1**/**11**)$_{frag}$ (Figure 9c) and TS(**3**/**12**)$_{frag}$ (Figure 9d). Nonclassical three-center two-electron (3C2E) bonding arises from intramolecular $\pi \rightarrow$ p electron donation. Finally, the ostensible H atom-bridged TS **12** does not involve a hydride migration. Instead, TS animation of the $\nu/c = 201i$ cm^{-1} vibrational normal mode (Figure 3l) shows H atom wagging. The IRC for this motion was limited and inconclusive

since it did not lead to a 1,2-H atom shift TS or a 1,2-C atom shift TS that would ultimately give enyne **11**.

■ CONCLUSIONS

Inherent characteristics of tricyclo[2.1.0.0^{2,5}]pent-3-ylidene (**1**) were computed using DFT. The divalent C atom of singlet **1** is stabilized by nonclassical electron delocalization from flanking bent bonds comprising well-aligned σ/π-type orbitals. This interaction is responsible for the singlet carbene's bent C_s-symmetric structure. Its main bridge is tilted ±43.5 deg from a C_{2v}-symmetric geometry, which triplet **1** and the bridge-flapping TS do have. The energy barrier for flapping ($E_a = 17.0$ kcal/mol) is much higher than that computed for adamantylidene ($E_a = 1.1$ kcal/mol), whose main bridge is tilted only ±19.7 deg from a C_{2v}-symmetric geometry. Thus, bridge-flapping conformerism within singlet **1** is relatively slow.

The sizeable ΔE_{S-T} (-44.9 kcal/mol) and gas-phase PA (258 kcal/mol) values computed for **1** suggest that the singlet is nucleophilic. This is further supported by a 2-D philicity chart of tabulated $\Delta\Delta E$ values obtained from the frontier MO energies of singlet **1** and representative sets of carbenes and alkenes. Computations reveal that singlet **1** will react more quickly and completely with electron-poor alkenes than with electron-rich alkenes.

When singlet **1** is substituted at C1, the corresponding carbene **1**-R adopts a proximal conformation as the divalent C atom leans toward C1 and a distal one as it bends toward C5. The thermodynamic preference for a *prox* or *dist* conformation depends on the σ inductive effect of the R-group. A proximal conformation is preferred when R is an EDG, while a distal one is favored when R is an EWG. This controllable stereo-electronic behavior parallels that for γ-adamantylidenes, which consequently undergo intramolecular and intermolecular reactions with high diastereoselectivity.

Rearrangements of polar carbene **1** were investigated. The formation of pyramidane (**2**) via a 1,3-C−H bond insertion TS or via a 1,3-zwitterionic TS was conclusively proven by their IRCs. That for **1 → 2** is very flat and requires a supplemental geometry optimization to reach **2**. Formation of tricyclo-[2.1.0.0^{2,5}]pent-2-ene (**3**) via [1,2]-sigmatropic transformations of **1**, for example, is unlikely since bridgehead alkenes have high strain energies. The IRC computed for bridge-flapping within **3** was found to be identical to that for *transverse* bridge-flapping within **1**. Hence, **1** and **3** are the same molecule. This is seen from their shared ylidic resonance form, which increases in importance as carbene nucleophilicity increases, as with NHCs. Although TS(**3**/**3**)$_{flap}$ violates Bredt's rule, strain is mitigated during *transverse* bridge-flapping within **1** by a lengthening of the cyclopropane unit's C−C bonds to 1.678 Å.

The enyne fragmentation of singlet **1** was also modeled. An IRC analysis of the enyne TS showed that the elementary step *begins* from a TS—that for singlet **1** bridge-flapping. Thus, the C_{2v}-symmetric TS is a *shared* TS and bifurcation point. Such stringent orbital alignment will preclude enyne formation in the case of **1**.

Overall, the results anticipate that **1** is a nonclassically delocalized carbene. Its electron lone pair is a source of substantial Lewis basicity, making the carbene as nucleophilic as most NHCs. The carbene will react faster and more completely with electron-poor alkenes than with electron-rich ones. Also, its 1-substituted derivatives are subject to stereoelectronic control in a similar way as for *γ*-substituted adamantylidenes. Finally, carbene **1** and bridgehead alkene **3** are the same entity. They have the same set of Cartesian coordinates despite having different Lewis structures.

COMPUTATIONAL METHODS

Quantum chemical calculations were performed using the Spartan'14 Parallel Suite (v. 1.1.8) computer program.[111] The restricted or unrestricted SCF wave functions of molecular equilibrium geometries and transition states were computed using the DFT method (U)MPWB1K[112] with a 6-311G(d) basis set. Frozen-core second-order Møller−Plesset perturbation theory (MP2(fc)) with a 6-31G(d) basis set was used to check earlier works.[5,73] Normal-mode vibrational analyses were performed at the level of geometry optimization. The harmonic frequencies were used to obtain temperature-independent zero-point vibrational energy (E_{ZPVE})[113] and temperature-dependent thermal vibrational energy ($\Delta_{vib}H$) values. Each reaction transition state (TS) had one, and only one, imaginary frequency ν/c whose normal mode was animated to verify the motions expected for the elementary step. Intrinsic reaction coordinates (IRCs) were subsequently generated to follow conformational bridge-flapping, enyne fragmentation, etc. Single-point energy (E) values were computed using the (U)MPWB1K/cc-pVTZ theoretical model. All E_{ZPVE} values were scaled by $z = 0.9513$[114] before being added to E ($T = 0$ K; $p = 0$ atm). Relative energy values ($\Delta_{rel}E$) are specified with regard to tricyclo[2.1.0.0^{2,5}]pent-3-ylidene, the 1-substituted carbene's proximal conformer, etc., which were set equal to [0]. Conversion of E values to enthalpy (H_T) values was done according to eq S1 (see the Supporting Information; computational standard state: $T = 298.15$ K; $p = 1$ atm; cf. Table S1). All $\Delta_{vib}H$ values were scaled by H = 0.9462[114] before being added to the ZPVE-corrected E values. The increase in kinetic energy, due to translations (3(1/2)RT) and rotations (3(1/2)RT), for each nonlinear molecule was then added. Finally, RT (i.e., "pV work" needed to expand 1 mol of ideal gas to $V = 24.465$ L at $T = 298.15$ K and $p = 1$ atm) was added to obtain H_T (eq S1).

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02414.

　Computational methods, Cartesian coordinates, and energies/enthalpies (PDF)

　Energy results/data (XLSX)

　Transition-state IRCs (XLSX)

　Conformer IRCs (XLSX)

　$\Delta\Delta E$ calculations (XLSX)

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Notes

The authors declare no competing financial interest.

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